Removal of Chlorine Gas using Metal-Organic Frameworks

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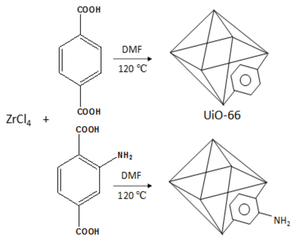
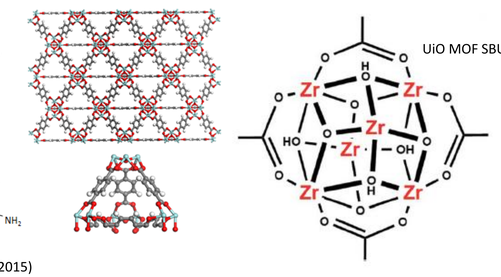
Introduction

Chlorine (Cl_2) gas has been a notable chemical weapon from its first use in World War I to its modern implementation in the Syrian civil war. Cl_2 is a significant threat due to the ease of obtaining it and its strong inhalation toxicity. Metal-organic frameworks (MOFs) are novel materials comprised of metal/metal oxide secondary building units (SBUs) connected by organic linkers. The large number of possible SBU/linker combinations allow for a MOF to be tailored to a wide spectrum of physical and chemical properties. Among these materials, the UiO MOFs, characterized by Zr_6O_6 SBUs linked together with benzene dicarboxylate analogs, are particularly notable due to their exceptional stability against a wide variety of pH, pressure, temperature, and humidity environments. The UiO analogue UiO-66-NH_2 in particular has generated high interest in air purification applications due to potential reactivity generated from its amine functionalization. This study investigated the reactivity of UiO-66-NH_2 against Cl_2.

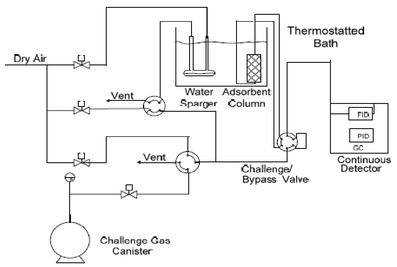


(DeCoste, 2015)

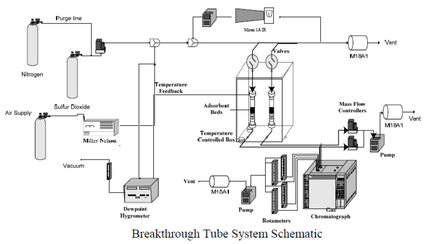


(Katz, 2015)

Experimental



Microbreakthrough System Schematic

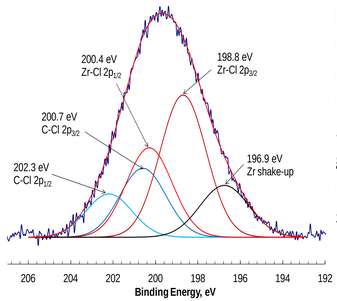


Breakthrough Tube System Schematic

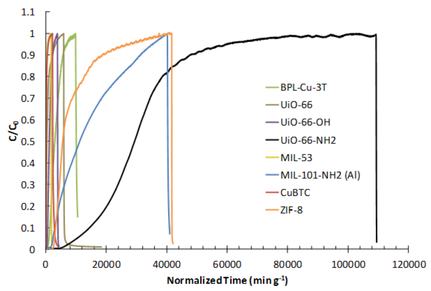
UiO-66-NH_2 was first evaluated for its baseline Cl_2 removal capabilities in a microbreakthrough system at 2000 mg/m3 challenge and total flow 20 mL/min and compared to several other MOFs that have shown a history of high adsorption capacity against toxic industrial chemicals. Engineered granules of the material were later evaluated in a breakthrough tube system at 2000 mg/m3 and 6.6 cm/s total flow and compared to 3M's Broad Spectrum Carbon (BSC), used to simulate activated carbons used in military filters. Samples were characterized via N_2 isotherm, XRD, FTIR, XPS, TGA, and ^1H NMR.

Approved for Public Release

Data



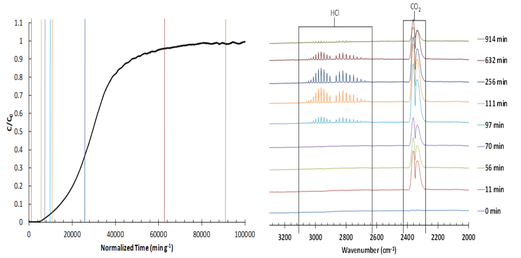
XPS of Cl_2-exposed UiO-66-NH_2 (DeCoste, 2015)



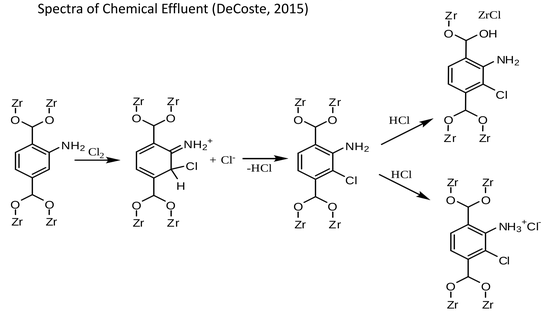
Microbreakthrough results have shown that UiO-66-NH_2 exhibited a higher capacity than other high-performance materials by nearly an order of magnitude against chlorine gas challenge, including 3M BSC. This material was able to absorb over 1 full gram of chlorine gas per gram of sorbent, an unprecedented standard in the PRO104 TIC screening program.

	Capacity (mol kg^{-1})	Capacity (g g^{-1})
BPL-Cu-3T	1.9	0.13
UiO-66	0.4	0.03
UiO-66-OH	0.7	0.05
UiO-66-NH_2	17.5	1.24
MIL-53	0.1	0.01
MIL-101-NH_2 (Al)	8.0	0.56
Cu-BTC	0.1	0.01
ZIF-8	6.1	0.43
3M BSC	5.2	0.37

Mechanism



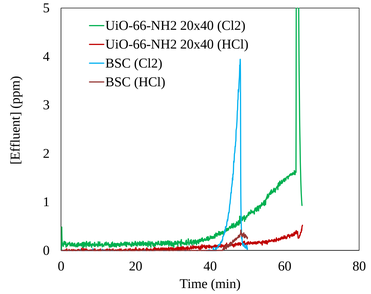
Cl_2 Microbreakthrough Results with Corresponding Time-Dependent FTIR Spectra of Chemical Effluent (DeCoste, 2015)



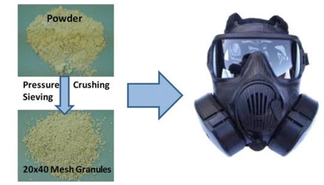
Chlorine removal on the UiO-66-NH_2 MOF was found to proceed via an ortho-para-substituting electrophilic aromatic substitution reaction aided by the amine group on the organic linker. HCl was formed as a byproduct of this process, and it eventually reacted with the linker-node junction of UiO-66-NH_2, forming a zirconium oxychloride-type species and decomposing the MOF.

Engineering

For filter applications, a material must be engineered in a granulated form to avoid issues with pressure drop and dusting that cannot be overcome with a powder. This inevitably leads to a diminished performance of the material against chemicals of interest due to loss of effective surface area and potential blocking of reaction sites upon pelletization. UiO-66-NH_2 maintained its chlorine removal capabilities reasonably well after pelletization, however, and still performed on par with 3M BSC.



Cl_2 Breakthrough Tube Results



UiO-66-NH_2 Powder and Granule Forms

Parameter	BSC	UiO-66-NH_2
Cl2 break time	44.4	46.4
Cl2 loading (g/g)	0.37	0.39
HCl break time	73.0	75.1
HCl loading (g/g)	0.61	0.63

Conclusions & Path Forward

UiO-66-NH_2 has shown unprecedented chlorine removal capabilities not approached by any other sorbent. We plan to transition this material into prototype M61 JSGPM filters. We are also investigating the growth of this MOF on various fabrics for escape-type respirators and protective suits.

References

DeCoste, J.B.; Browe, M.A.; Wagner, G.W.; Rossin, J.A.; Peterson, G.W. "Removal of Chlorine Gas by an Amine Functionalized Metal-Organic Framework via Electrophilic Aromatic Substitution" *Chemical Communications* (2015), submitted

Katz, M.J.; Moon, S.Y.; Mondloch, J.E.; Beyzavi, M.H.; Stephenson, C.J.; Hupp, J.T.; Farha, O.K. "Exploiting parameter space in MOFs: a 20-fold enhancement of phosphate-ester hydrolysis with UiO-66-NH2" *Chemical Science* (2015), 6, 2286

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